

Patent Laid-Open No.8-133789

Laid-Open Date: May 28, 1996

Application No.: Patent Application No. 6-267090

Application Date: October 31, 1994

Applicant: Central Glass Co., Ltd.

Inventors: Tsuyoshi Kondo, Toshikazu Nagashima and

Haruki Kuramasu

Representative: Patent attorney: Eiichi Sakamoto

[Title of Invention]

Ultraviolet absorption transparent material

[Abstract]

[Object] An ultraviolet absorption transparent material, which is excellent in the optical characteristics, can shade ultraviolet rays in a state of colorless and transparent, and in particular, can especially sharply shade the boundary of the ultraviolet/visible region near 400 nm, and is excellent in the adhesion, the chemical resistance, the marring resistance, and the durability, and can be used as windows for motorcars for a long period of time, is obtained by a low-temperature curing type treatment.

[Construction] An ultraviolet absorption transparent material obtained by coating a solution of a polysilazane-base mixture and film-forming on the surface of a hard coat type ultraviolet absorption film formed after coating a synthetic resin-base primer coating solution added with the solution of a fluorescent brightening agent and an ultraviolet absorbent on a transparent base material followed by heat-curing to form an ultraviolet absorbing thin film, by successively coating a silicone-base hard coating solution of a siloxane prepolymer dissolved in an organic solvent and curing by heating to form a protective thin film.

[Claims]

[Claim 1] An ultraviolet absorption transparent material characterized by coating and film-forming a solution of a polysilazane-base solution on the surface of a hard coat type ultraviolet absorption film formed by successively coating, after coating a synthetic resin-base primer coating solution added with the solution of a fluorescent brightening agent and an ultraviolet absorbent on the surface of a transparent base material followed by heat-curing to form an ultraviolet absorbing thin film, by coating a silicone-base hard coating solution formed by dissolving a siloxane prepolymer in an organic solvent followed by heat-curing to form a protective thin film.

[Claim 2] The ultraviolet absorption transparent material described in claim 1 wherein the above-described

synthetic resin-base primer coating solution is an acrylic primer coating solution.

[Claim 3] The ultraviolet absorption transparent material described in claim 1 or 2 wherein the above-described ultraviolet absorbent contains at least an indole-base compound.

[Claim 4] The ultraviolet absorption transparent material described in claims 1 to 3 wherein the above-described polysilazane-base mixture is a low-temperature curing type polysilazane-base mixture.

[Claim 5] The ultraviolet absorption transparent material described in claim 4 wherein the above-described low-temperature curing type polysilazane-base mixture is a mixture containing a poly(perhydrazane)-base as the main component.

[Detailed Description of the Invention]

[0001]

[Industrial Field of Application] The present invention is a transparent material coated with a coating film excellent in the ultraviolet absorbing property, and further relates to an ultraviolet absorption material, which has a higher abrasion resistance and durability than the case of using a single plate, while maintaining various characteristics.

[0002] The material is an ultraviolet absorption transparent material useful for various kinds of window materials of, for example, buildings, houses, vehicles, vessels, airplanes, and further various display instruments, etc., and particularly, windows of motorcars, as ultraviolet shading filter members.

[0003]

[Prior arts and its Problems] Hitherto, as the treatment method of generally imparting the ultraviolet absorbing property to a transparent material such as a glass base, there are followings.

[0004] First, there is, a method of compounding a transparent material itself with an ultraviolet absorbing compound, for example, there are various glass compositions each obtained by melt-adding a metal compound into a glass (e.g., Japanese Patent Laid-Open No. 47812/1977) and various resin films each obtained by adding by dispersion an ultraviolet absorbent in a resin film (e.g., Japanese Utility Model Laid-Open No. 17925/1984). However, they are unsuitable for the small amount many kinds production, the product, wherein the absorption wavelength reaches the boundary (e.g., about 400 nm) of the ultraviolet/visible region, is liable to form coloring and fog of the film, etc., a technique is required to make colorless, and it is hard to say that the control is always easy.

[0005] Also, there is a method of sticking an ultraviolet absorbing transparent film to the surface of a transparent material. For example, there is a laminated glass obtained by

inserting a polyvinyl butyral intermediate film and the like containing an ultraviolet absorbent between glass sheets (e.g., Japanese Patent Laid-Open No. 32352/1981). However, the chemical resistance, the marring resistance, the durability, coloring and fog are improved comparing to the case of single resin film, but the form correspondence is bad and the thickness becomes considerably thick and the product is hard to become light weight.

[0006] Furthermore, there is a method of forming an ultraviolet absorbing transparent film on the surface of a transparent material. For example, by applying a vapor phase film-forming method such as sputtering onto a base material which is a transparent material (e.g., Japanese Patent Laid-Open No. 76083/1992), or a liquid phase film-forming method such as sol-gel, (e.g., Japanese Patent Laid-Open No. 97103/1992). However, a large amount of an organic compound, which is liable to be decomposed, cannot be used, since the inorganic compound becomes an absorption base, ultraviolet rays cannot be sufficiently sharply cut up to the boundary (about 400 nm) of the ultraviolet/visible region, and also, since for forming film, raising of the temperature of the base and burning thereof are inevitable, the methods can be applied only to a base having a heat resistance. Furthermore, by only the organic resin coating film containing a large amount of a simple ultraviolet absorbent, the product becomes inferior in the chemical resistance, the marring resistance, and the durability.

[0007] Also, in a resin base material, there is a method of obtaining a transparent synthetic resin sheet, which cuts at least 90% ultraviolet rays and has a visible light transmittance of at least 80%, by a high-temperature high-pressure dyeing method or a normal pressure carrier method utilizing a dispersion type fluorescent paint having a brightening action, for example, 2,5-bis(5'-tertiary butylbenzoxazolyl)thiophene, etc., is known (e.g., Japanese Patent Laid-Open No. 126503/1986). However, in the case, ultraviolet rays are shaded by absorbing without using an ultraviolet absorbent, and the transparency is excellent, but, in particular, actually, fluorescence becomes too remarkable, and the durability is considerably inferior for practical use.

[0008] In these circumstances, in Japanese Patent Laid-Open No. 145387/1994 already filed by the present applicant, an ultraviolet absorption transparent material prepared by forming an ultraviolet absorbing thin film with a synthetic resin-base primer coating solution containing an fluorescent brightening agent and an ultraviolet absorbent, and coating a specific silicone-base hard coating protective thin film on the surface of the ultraviolet absorbing thin film was proposed, which

could be sufficiently used without troubles except the case of being used in a severe environment such as the case of sliding-contact for a long period, and could very sharply shade the boundary of the ultraviolet/visible region in near 400 nm.

[0009] On the other hand, hitherto, various kinds of silazanes have been used for various uses, and in these materials, as the materials relating the surface improvement of so-called articles, there are following materials. For example, in Japanese Patent Laid-Open No. 138107/1989 there are disclosed a modified polysilazane, the production method and the uses thereof, and it is described to prepare a solution comprised of a raw material polysilazane using perhydropolysilazane as the starting material, an ortho-xylene as a solvent, and a silicon carbide as a filler and a product obtained by coating the solution of an SUS base plate followed by forming film.

[0010] Also, for example, Japanese Patent Laid-Open No. 311120/1993 discloses a composition for forming a protective film of an ultraviolet shading glass and an ultraviolet shading glass, and an ultraviolet shading glass obtained by coating on the surface of a glass coated with an ultraviolet shading film of ZnO or TiO<sub>2</sub>, etc., with a composition for forming protective film containing a polysilazane having between (number of Si-H bonds of SiH<sub>4</sub> group)/(the number of all the Si-H bonds) = 0.13 to 0.45, and having a number average molecular weight of from 200 to 100,000 as the indispensable component and diluted with a solvent such as xylene is described.

[0011] Furthermore, for example, in Japanese Patent Laid-Open No. 310444/1993, a water-repellent product and the production method thereof are disclosed and, for example, a product comprised of a base material, a silicon dioxide-containing coated film formed by reacting an SiH<sub>4</sub> gas, an N<sub>2</sub> gas for separation, and an O<sub>2</sub> gas on the surface of a base material, and a water-repellent layer formed on the coated film and made of a nitrogen analog of a polysiloxane such as, for example, hexamethyldisilazane, etc., or a fluorine-containing disilazane-base organic silazanes compound is described.

[0012] Furthermore, for example, in Japanese Patent Laid-Open No. 163174/1993 already filed by the present applicant, an ultraviolet shading glass for vehicles is disclosed, and the product is obtained by forming at least one layer of an ultraviolet shading film on a glass and forming thereon a layer containing silicon, for example, by coating thereon a compound having at least a CH<sub>3</sub>-Si bond and/or a compound having an Si-N bond is described.

[0013]

[Problems that the Invention is to Solve] As described above, in the ultraviolet absorption transparent material described in, for example, the above-described Japanese Patent Laid-Open

No. 145387/1994, etc., particularly, the ultraviolet absorbing property, the abrasion resistance, the chemical resistance, the weather resistance, etc., are greatly improved, and the product can be used at any places or in any environments, but these products were not always sufficiently insure for the safe use as the products without causing damage or deterioration giving a hindrance after using for a long period, for example, for from half a year to about one year in a severer environment than a sliding contact, etc., such as, for example, as window glasses of motorcars, such as front glasses, rear glasses, side door glasses vertically moving, etc.

[0014] On the other hand, the ultraviolet shading glass for vehicles described, for example, in the above-described Japanese Patent Laid-Open No. 163174/1993 surly has the excellent ultraviolet shading property and also the excellent marring resistance and weather resistance to the vertical moving of windows and scratches and rubbing but in the case of employing as the relatively low temperature curing type ultraviolet absorbing thin film as shown by the ultraviolet absorption transparent material described in the above-described Japanese Patent Laid-Open No. 145387/1994, the above-described ultraviolet shading glass cannot be always employed as it is.

[0015] Also, similarly, for example, according to the modified polysilazane, the production method and the uses thereof described in the above-described Japanese Patent Laid-Open No. 138107/1999, it is hard to say that the product is the above-described relatively low-temperature curing type and cannot be employed for the relatively low-temperature curing type described in the above-described Japanese Patent Laid-Open No. 145387/1994 as well as cannot be employed as a transparent material which is required to have a sufficient transparency.

[0016] Furthermore, for example, the composition for forming an ultraviolet shading glass protective film and the ultraviolet shading glass described in the above-described Japanese Patent Laid-Open No. 311120/1993 cannot be similarly employed for the relatively low-temperature curing type described in the above-described Japanese Patent Laid-Open No. 145387/1994.

[0017] Moreover, for example, in the water-repellent article and the production method thereof described in Japanese Patent Laid-Open No. 310444/1993, a silicon dioxide coated film is used as the under layer of a glass surface and an organic silazane compound is coated thereon as a silazane-base water-repellent, and the method cannot be employed by no means for the technique described in the above-described Japanese Patent Laid-Open No. 145387/1994 in which the relatively low-temperature curing type ultraviolet absorption thin film is used as the under layer, which is hard coated.

[0018]

[Means for Solving the Problems] The present invention has been made in view of the problems of prior art and it is an object of the invention to provide an useful ultraviolet absorption transparent material, in which for very sharply cutting the boundary of the ultraviolet/visible region, a fluorescent brightening having an absorption near the boulder and an ultraviolet absorbent are used together, and a fluorescence can be prevented and coloring caused by using a large amount of an ultraviolet absorbent can be prevented; by mixing them, a synthetic resin-base primer composition having a good adhesion to the surface of a transparent base material is prepared to provide a coating solution which can form a film at a relatively low temperature; by further protecting the film thus formed with a silicone-base hard coating film, and by further forming film by coating a solution of a polysilazane-base mixture, ultraviolet rays are sharply shaded near 400 nm; and while maintaining the excellent chemical resistance, the marring resistance, and the durability capable of being used as external cladding, especially the abrasion resistance, marring resistance and durability are remarkably excellent even under various severe conditions is provided.

[0019] That is, the present invention provides an ultraviolet absorption transparent material characterized by coating and film-forming a solution of a polysilazane-base solution on the surface of a hard coat type ultraviolet absorption film formed by successively coating, after coating a synthetic resin-base primer coating solution added with the solution of an fluorescent brightening agent and a ultraviolet absorbent followed by heat-curing to form an ultraviolet absorbing thin film on the surface of a transparent base material, by coating a silicone-base hard coating solution formed by dissolving a siloxane prepolymer in an organic solvent followed by heat-curing to form a protective thin film.

[0020] Also, the invention provides the above-described ultraviolet absorption transparent material characterized in that the above-described synthetic resin primer coating solution is an acrylic primer coating solution. And also, the invention provides the ultraviolet absorption transparent material characterized in that the above-described ultraviolet absorbent contains at least an indole-base compound.

[0021] Furthermore, the invention provides the above-described ultraviolet absorption transparent material characterized by that the above-described polysilazane-base mixture is a low-temperature curing type polysilazane-base mixture. Moreover, the invention provides the ultraviolet absorption transparent material characterized in that the above-described low-temperature curing type polysilazane-base mixture is the

mixture containing poly(perhydrazane)-base as the main component.

[0022] Now, as described above, the above-described fluorescent brightening agent may be any materials as long as which absorb in the ultraviolet region, emit a fluorescence in the visible region, can be melt-added to a synthetic resin-base primer, particularly to an acrylic primer coating agent, and does not change the coated film thereof by heat-curing at a relatively low temperature, including, for example, UVITEX-OB (2,5bis(5'-tertiarybutylbenzoxazole)thiophen, 2-(3,5-di-t-butyl-2-hydroxyphenyl)-5-chlorobenzotrizole, manufactured by Ciba-Geigy Corporation) and EB-501 (manufactured by Mitsui Toatsu Senryo K.K.), etc., which has a proper heat resistance and in which the absorption wavelength is in the ultraviolet/visible region boundary (e.g., about 400 nm).

[0023] Also, the addition amount of, for example, the above-described UVITEX-OB is from about 0.02 to 0.5% by weight. When the addition amount thereof is less than 0.02% by weight, the effect thereof is not obtained, while when the addition amount exceeds 0.5% by weight, the concentration becomes near the limit of the solubility and the recrystallization occurs to liable to cause a coated film defect, and also the addition of more than necessary becomes uneconomical.

[0024] Also, as the above-described ultraviolet absorbent, which is used together with the above-described fluorescent brightening agent, there are, for example, a benzophenone-base, a benzotriazole-base, a benzoate-base, a cyano acrylate-base, and a salicylate-base, and there are TINUVIN 327 (manufactured by Ciba-Geigy Corporation), NIOSORB 100 (2,4-dihydroxybenzophenone, manufactured by Kyodo Yakuhin K.K.), SEESORB 706 (2-(2'-hydroxy-5'-methyl-3'-(3",4",5",6"-tetrahydrophthalimidylmethylphenyl)benzotriazole, manufactured by Shipro Kasei K.K.), and SEESORB 712 (2,4-di-t-butylphenyl-3'5' - di-t-butyl- 4'-hydroxy benzoate, manufactured by Shipro Kasei K.K.), and also, as the indole-base compound, for example, BONASORB-UA3901 (manufactured by Orient Kagaku K.K.) is contained and particularly, the absorption wavelength thereof has the effect in the ultraviolet/visible region boundary (e.g., about 400 nm).

[0025] Also, the addition amounts of, for example, the above-described TINUVIN 327, NIOSORB 100, and SEESORB 706 and 712 are from about 0.1 to 1.5% by weight. When the addition amounts are less than 0.1% by weight, the effect thereof is not obtained, and when the addition amounts exceed 1.5% by weight, the concentration becomes near the limit of the solubility and the recrystallization occurs to liable to cause a coated film defect, and the addition of more than necessary becomes uneconomical. Also, the addition amount of, for example, the

above-described BONASORB-UA3901 is from 0.02 to 0.3% by weight, when the addition amount is less than 0.02% by weight, the effect thereof is not obtained and when the addition amount exceeds 0.3% by weight, the coated film becomes yellowish, which becomes gradually remarkable.

[0026] The using ratio of the fluorescent brightening agent and the ultraviolet absorbents is from about 1 : 0.5 to 1 : 3.0 by mol ratio (about 1 : 0.5 to 1 : 10 by weight ratio), and preferably from about 1 : 1 by mol ratio (preferably from about 1 : 3 to 6 by weight ratio). When the content of the fluorescent brightening agent becomes larger, the see-through is deteriorated by fluorescence, and when the content thereof is too less, the desired ultraviolet absorbing power is not obtained.

[0027] Furthermore, about the synthetic resin primer, particularly the acrylic primer, since it is necessary to sufficiently dissolve the above-described fluorescent brightening agent and ultraviolet absorbent, it is better to use a mixed solvent of a combination of an ether alcohol-base solvent such as ethyl cellosolve, etc., and a ketone alcohol-base solvent such as diacetone alcohol, etc., or a ketone, an ether, or an aromatic solvent for considering that the transparent base material is not damaged. Particularly, in the case of using a glass sheet form materials, etc., as the transparent base material, a ketone-base solvent such as cyclohexanone having a dissolving power is preferred.

[0028] Furthermore, as the above-described synthetic resin, there are, for example, acrylic resins, urethane-base resins, fluorine-base resins, polyester-base resins, etc., and in these resins, as the above-described acrylic resin, by utilizing a commercially available acrylic resin, for example, Dianal BR 88, 85, or 80 (manufactured by Mitsubishi Rayon Co., Ltd.), etc., the coating solution may be prepared by the relations of concentration, viscosity, or a film thickness. It is preferred that the concentration of the resin component is from about 1 to 15% by weight, the total concentration of the fluorescent brightening agent and the ultraviolet absorbent is from about 0.5 to 2% by weight, the viscosity is from about 10 to 500 cp, and further, the film thickness is from 1 to 10  $\mu$ , more preferably, from about 2 to 8  $\mu$ . In particular, the thickness of the topcoat is about 3  $\mu$ , and the sum total film thickness is from about 5 to 11  $\mu$ .

[0029] In addition, when the transparent base material is a glass-made base material, to improve the adhesion, it is better to utilize an adhesion-improving agent such as a silane coupling agent and it is preferred to add, for example, OS808A (silicone-modified acrylic resin, manufactured by Daihachi



Chemical Industry Co., Ltd.), etc., in an amount of from about 1/4 to 1/2 of the resin component concentration. The addition amount thereof is from about 1 to 20% by weight. When the addition amount is too less, the effect is not obtained, and when the addition amount is too much, it becomes uneconomical.

[0030] Still further, the above-described ultraviolet absorbing synthetic resin primer, particularly the above-described ultraviolet absorbing acrylic primer is coated by, for example, a dipping method, a spraying method, a flow coating method, a spin coating method, or a printing method, etc., to form a film having a uniform thickness, and the coated film is dried by heating at a temperature of at least about 80°C for about one hour. When heating is insufficient, the primer component elates onto the protective film, which is a silicone-base hard coat, whereby, for example, fog, cracks, or the like are liable to cause, and when heating becomes excessive, the adhesion of the protective film, which is the silicone-base hard coat, is deteriorated.

[0031] Also, as the above-described silicone-base hard coating solution, fundamentally, a solution using an alcohol solution of a siloxane prepolymer obtained by hydrolyzing an organoalkoxysilane as the base is preferred, and, for example, a liquid containing a colloidal silica such as the coating composition described in Japanese Patent Laid-Open No. 220531/1987 already proposed by the present applicant is excellent in the marring resistance and is more preferred. In addition, as the commercially available products, for example, Tosguard 510 (manufactured by Toshiba Silicone Co., Ltd.) and Si Coat 2 (manufactured by Daihachi Chemical Industry Co., Ltd.) can be utilized.

[0032] Moreover, as the coating environment, for example, it is preferred that the temperature is from about 15 to 25°C, the humidity is from about 40 to 50 RH%, and further the clean extent is lower than about 10,000 in the point of preventing a coated film defect. Also, as the coating method, similarly to the case of the above-described ultraviolet absorbing synthetic resin primer, particularly the ultraviolet absorbing acrylic primer, a coating method giving a uniform film thickness, such as a dipping method, a spraying method, a flow coating method, a spin coating method, or a printing method can be utilized. The film thickness is preferably from about 2 to 5  $\mu$ . When the film thickness is thin, the surface protective effect is not obtained and when the thickness is thick, cracks are liable to cause while drying and curing by heating. Furthermore, for drying and curing by heating, a temperature of at least about 80°C is preferred, and particularly, when the transparent base material is a glass plate-form material, etc., the treatment at

a temperature of about 150°C for about two hours is preferred for increasing the surface hardness.

[0033] In addition, for improving the coating performance of the above-described ultraviolet absorbing acrylic primer or silicone-base hard coating solution, as a matter of course, a flow improving agent or a rheology-controlling agent may be properly added.

[0034] Furthermore, as the polysilazane-base mixture, a low-temperature curing type polysilazane-base mixture is preferred, and practically there is, for example, a mixture having a poly(perhydrosilazane)-base as the main component [for example, manufactured by TONEN CORPORATION], and in these mixtures, the mixture in which the solid component concentration in the solution is from about 5 to 40% by weight (rests being, for example, xylene, a curing catalyst, etc.) is preferably used.

[0035] Also, for forming the coated film of the mixture, a coating method of forming a uniform film thickness, such as a dipping method, a spraying method, a flow coating method, a spin coating method, or a printing method, etc., can be utilized, and the film thickness is from about 0.5 to 3  $\mu$ , and preferably from about 1.0 to 2.0  $\mu$ . When the thickness is thin, the effect of the surface protective strengthening becomes less and when the thickness is thick, cracks are liable to cause while drying and curing by heating and it becomes uneconomical. Furthermore, for drying and curing by heating, because the coated film contains the organic ultraviolet absorbent, fluorescent brightening agent, and resins, it is necessary to treat at a temperature of higher than about 100°C and lower than about 250°C, preferably, when the transparent base is a glass plate-form material, etc., the temperature is from about 150 to 220°C, and the treatment from about 10 to 60 minutes, and preferably for about 30 minutes is preferred for increasing the surface hardness. In addition, as the environment at coating, it is carried out in the air-conditioned environment that the temperature is about 25°C and the relative humidity at normal temperature of from about 20 to 50% RH, and preferably at about 10% RH.

[0036] Also, as the diluting solvent for the solution of the polysilazane-base mixture, there are, for example, aromatic compounds such as benzene, toluene, and xylene; ether compounds such as ethyl ether, and tetrahydrofuran (THF); chlorine compounds such as methylene chloride and carbon tetrachloride; and ketone compounds such as butyl carbitol acetate, etc.

[0037] Moreover, as the above-described transparent base material, a material having the heat resistance of, for example, at least about 80°C may be used, and there are preferably inorganic glasses and resin glasses such as PC,

PMMA, PET, etc., and regardless of inorganic and organic, there is no particular restriction on the form thereof, and various forms are used. Also about the size and the construction, for example, a bent plate glass is as a matter of course, various tempered glasses, strength-up glasses, flat plates, a single plate can be used, and composite glasses and laminated glasses can be, as a matter of course, applied.

[0038]

[Action] As described above, according to the present invention, since the invention is a transparent material obtained by further coating a solution of a polysilazane-base mixture on the surface of a hard-coat type ultraviolet absorption film formed by coating a coating film having a specific construction and excellent in the ultraviolet shading property using a primer solution containing a fluorescent brightening agent and an ultraviolet absorbent, and a sufficient protective film; a fluorescence of the fluorescent brightening agent is absorbed by the ultraviolet absorbent and thus the coated film of not striking can be formed at a relatively low temperature, the surface thereof becomes double protective films of the specific hard coat and the specific silica-base film obtained from the solution of a polysilazane-base mixture (for example, by the surface analysis of SIMS, etc., N remains at partial positions of the film, for example, at the coat adhered portions, etc.), and particularly, the boundary of the ultraviolet/visible region of near 400 nm can be sharply cut with transparent and without being colored; and since the double protective films are in addition to excellent in the adhesion, the chemical resistance, the marring resistance and durability, does not cause cracks, etc., even in the above-described specific silica-base film having a relatively thick film thickness and shows a high adhesion to the hard coat film by a low-temperature treatment, becomes dense even in an amorphous form, is hard as or higher than 9H in pencil hardness, and has improved film strength and smoothness; an ultraviolet absorption material which is greatly improved particularly in the abrasion resistance, marring resistance, and durability, can be used for external cladding such as buildings, houses, vehicles, and various kinds of window materials, and can be used for useful ultraviolet shading windows, and particularly can be used for front glasses, rear glasses, vertically moving side glasses, etc. of motorcars for a long period of time under the severer using conditions and environment, can be provided easily at a low cost by simple coating treatments, which are low-temperature curing treatments.

[0039]

[Examples] Then, the invention is practically explained by the following examples. However, the invention is not limited to these examples.

[0040] (Preparation of ultraviolet absorbing acrylic primer)  
[For glass coating]

In a round-bottom flask equipped with a stirrer and a circulator were placed 305 g of cyclohexanone and 221 g of propylene glycol monomethyl ether as solvents, and with stirring at room temperature was added 32.5 g of Dianal BR-88 or BR-85 (manufactured by Mitsubishi Rayon Co., Ltd.) as acrylic resin. Furthermore, while continuing stirring, 3.25 g of UVITEX-OB (manufactured by Ciba-Geigy Corporation) as a fluorescent brightening agent and 3.25 g of BONASORB-UA3901 (manufactured by Orient Kagaku K.K.), TINUVIN 327 (manufactured by Ciba-Geigy Corporation), VIOSORB 100 (manufactured by Kyodo Yakuin K.K.), SEESORB 706 (manufactured by Shipro Kasei K.K.), or SEESORB 712 (manufactured by Shipro Kasei K.K.) as an ultraviolet absorbent were properly added thereto, and after raising the temperature to about 95°C in an oil bath over a time of about 30 minutes, the mixture was maintained for about 30 minutes to completely dissolve the added components. Then, heating was stopped, the temperature was lowered to normal temperature, and 65 g of a silicone-modified acrylic resin, OS-808A was added followed by dissolving with stirring to obtain an ultraviolet absorbing acrylic primer for glass coating.

[0041] The ultraviolet absorbing acrylic primer solution was transparent and had solid components of from about 8 to 11% and a viscosity of from about 200 to 350 cp (25°C).

(Preparation of ultraviolet absorbing acrylic primer)  
[For resin coating]

In a round-bottom flask equipped with a stirrer and a circulator were placed 58.5 g of cyclohexanone, 150 g of diacetone alcohol, and 390 g of propylene glycol monomethyl ether as solvents and with stirring at normal temperature, 45.5 g of Acryl BR-85 Resin (manufactured by Mitsubishi Rayon Co., Ltd.) was added thereto. Furthermore, while continuing stirring, 3.25 g of a fluorescent brightening agent, UVITEX-OB (manufactured by Ciba-Geigy Corporation) and 3.25 g of an ultraviolet absorbent, BONASORB-UA3901 (manufactured by Orient Kagaku K.K.) or TINUVIN 327 (manufactured by Ciba-Geigy Corporation) were added thereto, and after raising the temperature to about 95°C in an oil bath over a time of about 30 minutes, the mixture was maintained for about 30 minutes to completely dissolve the added components to obtain an ultraviolet absorbing acrylic primer for resin coating.

[0042] The ultraviolet absorbing acrylic primer solution was transparent and had solid components of from about 2 to 8% and a viscosity of about 35 cp (25°C).

(Preparation of silicone-base hard coating solution)

In a 500 ml round-bottom flask equipped with a stirrer and a circulator were placed 100 g of methyl triethoxysilane and 10 g of 3-glycidoxypopyl trimethoxysilane, after adding thereto 0.04 g of phthalic anhydride, the mixture was heated to about 40°C in a warm water bath to dissolve the components. Thereafter, 100 g of a weak basic colloidal silica aqueous solution, Snow Tex C (manufactured by Nissan Chemical Industries, Ltd., mean particle size of about 15  $\mu$ m, SiO<sub>2</sub> content of about 20%) was added, and the reaction was carried out at about 40°C for about 5 days. A composition having number average molecular weight by GPC (ULC 802A, manufactured by TOSOH CORPORATION) of about 1100 and solid components of about 29% was obtained. To the composition was added 145 g of isopropyl alcohol, the mixture was concentrated by a ultrafilter of fraction molecular weight of 1000 (manufactured by Nippon Millipore Co.) to obtain a composition of a number average molecular weight by GPC of about 1200 and solid components of about 20%. By adding about 0.1 part of dicyandiamide to the composition as a curing catalyst, a silicone-base hard coating composition was obtained.

[0043] (Preparation of polysilazane-base mixture solution)

To a mixture made of poly(perhydrosilazane) as the main component, a curing catalyst, etc., were added, and using xylene as a diluting catalyst, a solution having solid component concentration of about 20% by weight was obtained.

[Polysilazane manufactured by TONEN CORPORATION]

(Performance evaluation method)

Ultraviolet absorption: The absorption spectral pattern was measured by an ultraviolet/visible spectrometer.

[0044]

Fluorescent property: Visually observed under natural sunlight in the open air. (Anxious fluorescence, no fog.)

Abrasion resistance: According to JIS R 3221, truck wheel CS-10F, load 500 g.  $\Delta$ H (haze) value (%) after 1000 rotations.

[0045]

Hardness: Pencil hardness.

Adhesion: According to JIS K5400, cross-cut (1 mm square) tape releasing residue is shown by /100.

[0046]

Chemical resistance:

Acid resistance: 3 wt.% diluted H<sub>2</sub>SO<sub>4</sub>, 24 hrs.  
by immersion test.

Alkali resistance: 3 wt.% NaOH aqueous solution,  
24 hrs. by immersion test.  
Solvent resistance: 100% ethanol, 4 hrs. by spot  
test.

[0047]

Weather resistance: According to JIS D0205, the time until abnormalities (film cracks, releasing, remarkable yellowing) are visually observed by a sunshine carbon weather meter.

[0048] Example 1

A clear float glass base having a size of about 300 mm × 300 mm, and a thickness of about 3 mm was successively washed by a neutral detergent, water rinsing, and an alcohol, and after drying, wiped with acetone to provide a glass base for coating film.

[0049] One surface of the glass base for coating film was masked with a film, dipped in the ultraviolet absorbing acrylic primer solution for glass coating prepared as described above, pulled up at a speed of about 0.1 cm/sec., and dried at a temperature of about 120°C for about 0.5 hour to form an ultraviolet absorption film of about 6 μ in thickness.

[0050] Then, the glass base having the ultraviolet absorption film was dipped in the silicone-base hard coating solution prepared as described above, pulled up at a speed of about 1 cm/sec., and dried and cured at about 120°C for about 0.5 hour and at 150°C for about 0.5 hour to form a hard coat protective film of about 3 μ in thickness. The pencil hardness was about 7 to 8H.

[0051] Then, furthermore, in an air-conditioned clean room state of about 25°C and about 40% RH, the above-described glass base coated with the hard coat protective film was dipped in the polysilazane-base mixture solution prepared as described above and coated with the solution, followed by air-dried for about 10 minutes, then the coated glass base was placed in a hot-blast circulating drier at about 170°C for about 30 minutes to cure the coated film to obtained a silica-base film. The film was colorless transparent good film having no cracks and the film thickness thereof was about 1.1 μ. In addition, in the case of using a far infrared furnace, the coated film could be cured at about 200°C for about 15 minutes.

[0052] The obtained ultraviolet shading glass base, which was an ultraviolet absorption transparent material, was evaluated according to the above-described performance evaluation methods.

As the results thereof, the product was an ultraviolet absorption transparent material, which could shade ultraviolet

rays at a transmittance of 5% or lower in the wavelength of 400 nm or shorter, particularly could very sharply cut the boundary of the ultraviolet/visible region near 400 nm without being colored and with a sufficient see-through, could prevent the occurrences of striking emission phenomenon and fog, showed the excellent marring resistance as the haze value ( $\Delta H$ ) after taper test for the abrasion resistance being about 3.7%, had the weather resistance of at least 1000 hours without causing visual abnormality, showed no abnormality in the chemical resistance, and had the excellent durability. In addition, the pencil hardness was at least 9H.

[0053] Also, the product can be used for a long period of time in the case of being used as the window glasses such as the front glass, the rear glass, and the vertically moving side glasses of motor cars, and was greatly excellent in the marring resistance, the abrasion resistance, and the durability as compared with similar glasses of prior art.

[0054] Example 2

On the glass base as used in Example 1, using the primer solution as in Example 1 and by the film-forming same as Example 1, a similar ultraviolet absorption film of about 5  $\mu$  was formed.

[0055] Then, the glass base having the ultraviolet absorption film was dipped in Tosguard 510 (manufactured by Toshiba Silicone Co., Ltd.), which was a commercially available silicone-base hard coating solution, pulled up at a speed of about 1 cm/sec., and dried and cured at about 120°C for about 3 hours to form a protective film of about 3  $\mu$  in thickness. The pencil hardness was about 7H.

[0056] Moreover, in an air-conditioned clean room state of about 25°C and about 40% RH, the above-described glass base coated with the hard coat protective film was dipped in the polysilazane-base mixture solution prepared as described above and coated with the solution, followed by air-dried for about 10 minutes, then the coated glass base was placed in a hot-blast circulating drier at about 190°C for about 30 minutes to cure the coated film to obtained a silica-base film. The film was colorless transparent good film having no cracks and the film thickness thereof was about 1.4  $\mu$ .

[0057] The obtained ultraviolet shading glass base, which was an ultraviolet absorption transparent material, was evaluated in the same manner as Example 1. That product was a desired excellent ultraviolet absorption transparent material such that the characteristics such as shading of ultraviolet rays, were, as a matter of course excellent, as well as the above-described haze value ( $\Delta H$ ) was about 4.2%, the pencil hardness was at least 9H, etc.

[0058] Example 3

A PET film having a thickness of about 50  $\mu$  was dipped in the ultraviolet absorbing acrylic primer solution for resin coating described above, pulled up at a speed of about 0.1 cm/sec., and dried at about 120°C for about 0.5 hour to form an ultraviolet absorption film of about 5  $\mu$  in thickness.

[0059] Then, the film having the ultraviolet absorption film was dipped in the silicone-base hard coating solution prepared as described above, pulled up at a speed of about 1 cm/sec., and dried and cured at about 120°C for about 0.5 hour and at about 150°C for about 0.5 hour to form a protective layer of about 3  $\mu$  in thickness. The pencil hardness was from about 5 to 6H.

[0060] Moreover, in an air-conditioned clean room state of about 25°C and about 40% RH, the PET film coated with the hard coat protective film was dipped in the polysilazane-base mixture solution prepared as described above and coated with the solution, followed by air-dried for about 10 minutes, then, the coated PET film was placed in a hot-blast circulating drier at about 150°C for about 30 minutes to cure the coated film to obtain a silica-base film. The film was colorless transparent good film having no cracks and the film thickness thereof was about 1.2  $\mu$ .

[0061] The ultraviolet shading film, which was an ultraviolet absorption transparent material, obtained was evaluated as in Example 1. Particularly, the above-described haze-value ( $\Delta H$ ) became about 6.0%. and the resin film was a desired excellent ultraviolet absorption transparent material as in Example 1.

[0062] In addition, as described in Japanese Patent Laid-Open No. 328413/1993 already filed by the present applicant, the ultraviolet absorption transparent material obtained by combining an acrylic resin, a fluorescent brightening agent, an ultraviolet absorbent, solvent, and an adhesion improving agent at properly specified ratios, coating on a glass base an ultraviolet absorption film having a film thickness of from about 4 to 7  $\mu$  with solid components and the viscosity, coating thereon hard coat film as in the above-described examples, and further forming thereon a silica-base film as in the above examples was evaluated as in Example 1. As the results thereof, the formed material was a desired excellent ultraviolet absorption transparent material as in Example 1.

[0063] Comparative Example 1

On the glass base as in the above-described example was formed the ultraviolet absorption film as in the example without forming the hard coat film as formed in Example 1 and on the ultraviolet absorption film (in addition, the pencil



hardness of the film was about 1H) was formed a coated film with the polysilazane-base mixture solution as in Example 1 to form a silica-base film of about 1.5  $\mu$  in thick, whereby an ultraviolet absorbing glass base was obtained.

[0064] About the ultraviolet absorbing glass base obtained, in appearance, there were no cracks and the product was almost colorless and transparent in both the interior-of-a-room side and the outside, and the cutting property of ultraviolet rays near the wavelength of 400 nm and sharpness at the boundary of the ultraviolet/visible region were almost same as Example 1, but the surface pencil hardness was about 7H, and, for example, in the abrasion resistance, the haze value ( $\Delta H$ ) after taper test was about 32.8%, that is, the marring resistance and the abrasion resistance, etc., were inferior, and it was hard to say that the product was a desired ultraviolet absorption transparent material.

[0065]

[Effect of the Invention]

As described above, according to the present invention, a useful ultraviolet absorption transparent material, which is colorless and transparent, can shade ultraviolet rays, and particularly, very sharply cut ultraviolet rays at the boundary of the ultraviolet/visible region in the wavelength near 400 nm without reducing the optical characteristics, is excellent in the adhesion, the chemical resistance, the marring resistance and the durability, and further is equipped with more specifically excellent marring resistance, abrasion resistance and weather resistance, and can be widely employed in various fields, such as can be, as a matter of course, used for external cladding as window materials, etc., of buildings, houses, vehicles, etc., and can be used for a long period of time in sever using conditions and environments as window glasses such as front glasses, rear glasses, and vertically moving side door glasses of motorcars, can be provided easily at a low cost.